

**A PRELIMINARY MODEL FOR CORRELATION OF PLASMON RESONANCE SPECTRA
WITH ADHERENCE PROPERTIES OF CORROSION INHIBITORS
“VpCI-415”**

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ABSTRACT

Recent studies have shown that there is correlation between the effectiveness of additives containing corrosion inhibitors and surface plasmon resonance (SPR) spectra. In principle, SPR spectroscopy is a valuable tool to examine metal-inhibitor association because it is specifically sensitive to interface structure or electrochemical processes at a metal surface due to contact with water or an electrolyte solution. In this paper we present a preliminary design of a fiber-optic sensor system based on the use of SPR spectra to obtain quantitative information concerning metal-solution interface structure and electrochemical influences of the ambient environment. The sensor system presented employs an inverse model of the dependence of the SPR spectra on the molecular-polarization characteristics of surface deposits, for example inhibitor molecules, and the ambient environment. The potential extension of the inverse model and sensor geometry to the development of algorithms for signal analysis concerning fiber-optic-based corrosion sensors is discussed.

Keywords: corrosion inhibition, surface plasmon resonance spectroscopy, fiber-optic sensor, inverse modeling, metal-inhibitor interface structure

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1. REPORT DATE 01 MAY 2008		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE A Preliminary Model For Correlation Of Plasmon Resonance Spectra With Adherence Properties Of Corrosion INHmITORS				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Materials Science and Technology Division Naval Research Laboratory Washington, DC 20327				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 7	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

INTRODUCTION

In a series of studies we established a correlation between corrosion rates and general features of surface plasmon resonance (SPR) spectra.^{1,2,3} The analysis presented in those studies, although qualitative, demonstrated sufficient sensitivity of plasmon spectral features to the presence of inhibitors at a metal-salt-solution interface and the relative salinity. In this paper we present a preliminary fiber-optic sensor system based on the use of SPR response at a metal surface to obtain quantitative information concerning interface structure and the effects of electrochemical surface processes. This information can be used to assess inhibitor effectiveness and related corrosion levels. The system presented provides a general framework for elucidating the essential physical and algorithmic aspects of a fiber-optic based sensor utilizing surface plasmon resonance spectroscopy. This general framework is easily extendible to more complex fiber-optic sensor geometries and analyses of complex interface structure.

The simplest interpretation of the physical process underlying SPR is to consider surface plasmons as waves on a metal surface which propagate through a medium consisting of free electrons of a given density distribution and relative mobility. These surface waves result from the transfer of energy when an incident light beam of given wavelength is reflected off the metal. Any external influence tending to constrain the characteristic mobility of the surface electrons will interfere with the energy transfer and thereby dampen the surface plasmons. Because the electrochemical potential across a metal-solution interface influences the properties of surface electrons, there is a direct correlation between SPR response and electrochemical influences at the metal-ambient-solution interface.

A SIMPLE FIBER-OPTIC BASED SENSOR

In this section we present a simple fiber-optic sensor system, which will consist of a set of fiber-optic junctions whose geometry is that of the Kretschmann configuration for inducing surface plasmon resonance.⁴ Figure 1 shows a schematic drawing of a single fiber junction, which serves to demonstrate the basic design characteristics required of fiber-optic sensor systems utilizing SPR. The fiber-optic sensor system shown in Figure 1 consists of a junction interface between two optical fibers such that their cylindrical axes are arranged symmetrically about a given angle θ relative to a layer of gold coating deposited on the fibers at their juncture. The incident beam I_0 couples to the plasmon absorption channel associated with free electrons on the outer surface of the gold layer, which are in turn influenced by the interfacial structure and electrochemical environment. The polarity of the environment is therefore reflected in the differences between the input and output beams, $\Delta I = I_0 - I$, for a range of fiber junctions corresponding to a range of variation of the angle of incidence θ . It is significant to note that procedures for measurement of SPR spectra are essentially the same for both a fiber-optic guided light beam or an alternatively collimated specularly-reflected laser beam due to the geometric conditions of fixed angles of incidence and reflection for both types of arrangements.

AN INVERSE MODEL FOR SIGNAL ANALYSIS

In this section we present a simple inverse model for analysis of transmitted light signals modulated by their degree of coupling to surface plasmons at the metal interface. This model is defined by the three-phase interface system shown in Figure 2 and the system of equations

$$I = |R|^2, \quad R = \frac{(r_{01} + r_{12}X)}{(1 + r_{01}r_{12}X)}, \quad X = \exp[-2\pi i(d/D)], \quad D = (\lambda/2)(1/S_1), \quad (1)$$

$$r_{ab} = \frac{(\epsilon_b S_a - \epsilon_a S_b)}{(\epsilon_b S_a + \epsilon_a S_b)}, \quad S_i = (\epsilon_i - \epsilon_0 \sin^2 \theta)^{1/2}, \quad \epsilon_i = \epsilon_{iR} + i\epsilon_{iI} \quad (2)$$

where the quantities R , X , D , S_i and r_{ab} are functions of adjustable parameters, and I , d and λ are the reflected intensity, thickness of the metal film and wavelength of the incident light, respectively. These equations are based on the Fresnel formulation of the reflection coefficients for interfaces between homogeneous and isotropic media. This formulation is described in reference 5. The coefficient “ i ” in the above equations is the imaginary unit. The quantity r_{ab} is the Fresnel reflection coefficient. The quantities ϵ_0 , ϵ_1 and ϵ_2 are the complex dielectric functions of the optical fiber material, the material making up the single layer of thickness d , and the ambient medium, respectively. The angle of incidence θ is defined by Figures 1 and 2. The quantities ϵ_{iR} and ϵ_{iI} are the real and imaginary parts, respectively, of the dielectric constant ϵ_i and are such that

$$\epsilon_{iR} = n_i^2 - k_i^2 \quad \text{and} \quad \epsilon_{iI} = 2n_i k_i, \quad (3)$$

where the quantities n_i and k_i are the refractive index and extinction coefficient, respectively of the material indexed by “ i .” In the case of SPR the quantity k_i is significant in that it is characterized by relatively large values for angles θ at and about the region of resonance. In general this quantity is directly proportional to the absorption coefficient

$$\alpha = \frac{4\pi k}{\lambda} \quad (4)$$

where $I = I_0 \exp(-\alpha z)$ and z is the depth of penetration of the light into the substrate layer. A derivation of Eq.(4) is given on page 220 of reference 6. The extinction coefficient therefore provides a quantitative figure-of-merit of electrochemical forces at the sensor interface tending to constrain plasmon resonance response and correspondingly the degree of coupling of the input signal I_0 to the resonance absorption channel.

PROTOTYPE SENSOR MEASUREMENTS

Shown in Figure 3 are surface plasmon resonance spectra of a gold-coated substrate (a 50 nm gold film that was formed on cleaned cover glass by vacuum deposition). The curves represent: 1) a bare gold surface; 2) a gold surface in contact with an additive containing an unknown corrosion inhibitor; 3) a gold surface following rinsing of the additive with water; and 4) a gold surface following rinsing of the additive with 1% NaCl solution. These curves are of the reflected light intensity, I , as a function of angle of incidence of radiation (Figures 1 and 2). From the SPR results it is observed that a minimum occurs at an incident angle of about 46 degrees for the bare gold spectrum. When the gold surface is in contact with an additive solution the SPR minimum is observed to disappear. This damped response implies a change in the density distribution of surface electrons, which is sufficient for totally damping out any oscillations of the free electrons (surface plasmons) on the surface of the gold substrate. Such a response may be correlated with a surface containing a coating that tightly adheres to

the substrate and modifies the behavior of surface electrons. When the additive solution, is rinsed with water, and with 1% NaCl solution, the minimum, in the bare gold spectra, shifts to slightly higher values. Specific details of the experimental procedures have been described elsewhere.³ For the purposes of our present prototype analysis, the SPR curves shown in Figure 3, are of interest because their general features are exactly those that would be obtained by a set of fiber optic sensors, members of the set having the junction configuration, shown in Figure 1, at different angles θ .

PROTOTYPE ANALYSES AND DISCUSSION

The fiber-optic junction interface (Figure 1), the inverse model based on a three phase interface system (Figure 2) and the prototype SPR measurements (Figure 3) are sufficient for illustrating the essential physical and algorithmic aspects of a fiber-optic based sensor utilizing SPR spectroscopy. The relatively simple sensor system defined by the geometry shown in Figure 1 can be applied for analysis in different ways, ranging from qualitative to quantitative interpretations.

One mode of application of the prototype sensor system presented here is qualitative and involves comparison of the relative magnitudes of the signal I , corresponding to different ambient environments of the sensor interface. This type of analysis is equivalent to that presented previously for comparison of the effectiveness of inhibitor coatings.^{1,2,3} In practice this analysis would involve a collection of responses for a single fiber-optic junction (Figure 1) such that the angle θ is within the neighborhood of the resonance response, e.g., 46 degrees for the interface system whose spectra are shown in Figure 3.

Another mode of application, which is quantitative, involves optimization of inverse-model parameters with respect to the output signals $I(\theta)$ of the sensor system, i.e., Eqs.(1) through (3). In practice this analysis would involve a set of fiber-optic sensors (Figure 1) whose junctions define a set of angles θ spanning a relatively wide range of angles centered about the region of resonance response (see Figure 3). Optimization of the inverse-model parameters requires, in general, numerical methods employing optimization algorithms that iteratively adjust parameter values until a specified error tolerance is satisfied between the measured and calculated SPR spectra. For the purpose of the prototype analysis presented here, a relatively small set of adjustable parameters are considered, thus permitting parameter optimization to be undertaken interactively.

Referring to Figure 3, we observe estimates of the resonance amplitudes of 0.04, 0.08 and 0.13 for a bare gold substrate, additive-coated gold after water washing and additive-coated gold after washing with 1% NaCl solution, respectively. We consider parameter optimization only with respect to these amplitudes and according to adjustment of d and k_1 defined in Eqs.(1) through (3). The other parameters are assigned the fixed values $n_0=1.43$, $k_0=0.0$, $n_1=0.1726$, $n_2=1.0$, $k_2=0.0$ and $\lambda=633$ nm according to the experimental conditions and tabulated optical constants (n , k) for glass, gold and air.⁶ First, we consider adjustment of d and k_1 to values 54.5 nm and 3.42, respectively, such that there is good agreement between the measured and calculated resonance amplitudes for the case of the bare-gold substrate. For subsequent optimization the thickness parameter d is held fixed at 54.5 nm. This value is sufficient for constraining all the calculated resonance amplitudes to be within a very small neighborhood of the experimentally observed angles so that we may consider only the dependence of the resonance amplitudes on the value of the extinction parameter k_1 . For example, good agreement between the measured and calculated values of the resonance amplitudes for the water washed additive coated gold surface and 1% NaCl washed additive coated gold surface is obtained when d is fixed at 54.5 nm and k_1 is adjusted to 3.61 and 3.82, respectively. It is significant to note that the values of k_1 can be correlated with damping influences on free electrons at the interface occurring on an atomic

level. For example the classical Drude model (see page 263 in reference 6) establishes a relationship between k_1 and damping of charge motion on an atomic scale at the interface. Accordingly, the quantity k_1 can be related to a microscopic damping factor γ by an expression of the form $k_1 = C\gamma\lambda^3$ such that a free electron of effective mass m and charge e obtains a dipole moment ex as a result of interaction with a harmonically oscillating electric field E and is specified by the equation of motion

$$m \frac{d^2x}{dt^2} + m\gamma \frac{dx}{dt} = eE \quad (5)$$

Other types of microscopic influences such as surface roughness or inhomogeneities within a surface layer can be related to the macroscopic parameters n and k by extending the inverse model to systems having more than three phases and by relating dielectric constants to microscopic properties through the application of effective medium theories.⁵

CONCLUSIONS

Previously reported surface analysis demonstrated that additives containing inhibitors or electrolytic environments modify SPR responses at a metal surface. This qualitative analysis established the feasibility of using SPR spectroscopy for analysis of ambient corrosive environments and the effectiveness of inhibitor coatings. In this report we have presented a general framework for a fiber optic based sensor system that can be used to exploit the interfacial specificity of SPR spectra to study electrochemical processes and complex structures at a metal surface in solution. Such sensors could ultimately be engineered for use in a broad range of field applications directed at corrosion control. This general framework is potentially extendable to the analyses of complex interface structure because of the detailed characterization afforded by an inverse-model representation of physical processes affecting the output signals of the prototype sensor system.

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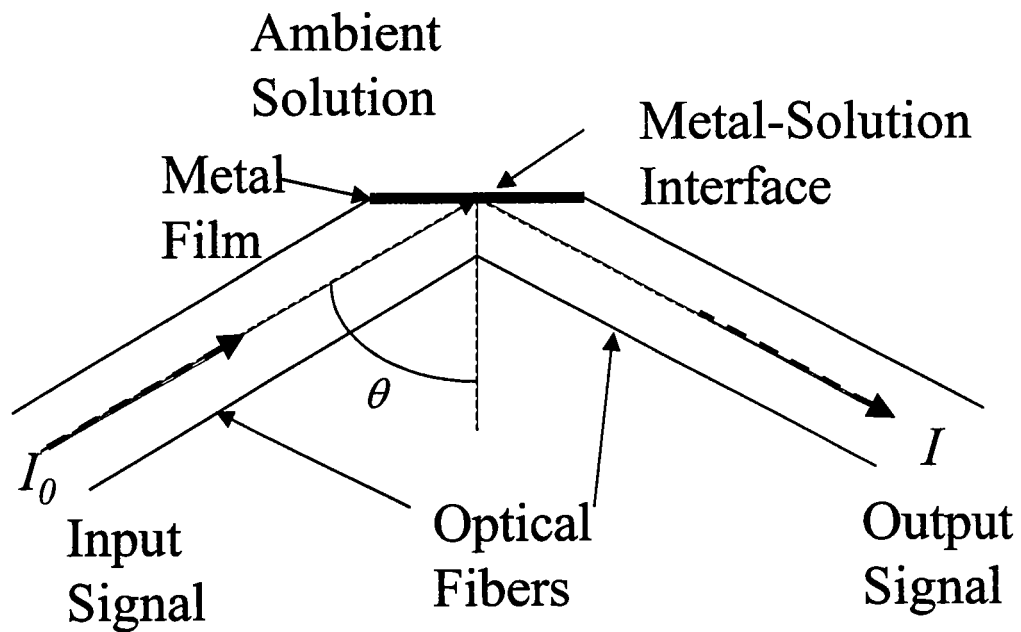


FIGURE 1: Schematic representation of a fiber-optic sensor configuration whose geometry is that of the Kretschmann configuration for inducing surface plasmon resonance.

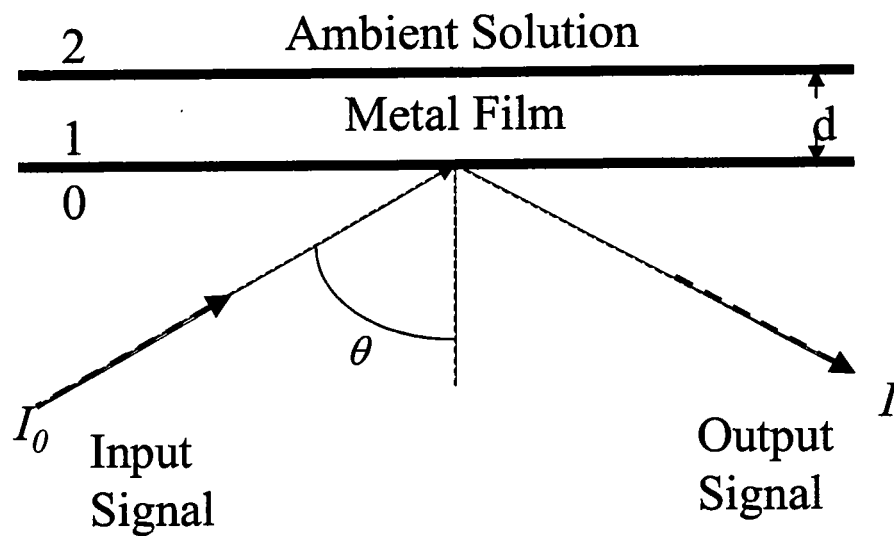


FIGURE 2: Schematic representation of a three-phase interface system represented by equations (1) through (3).

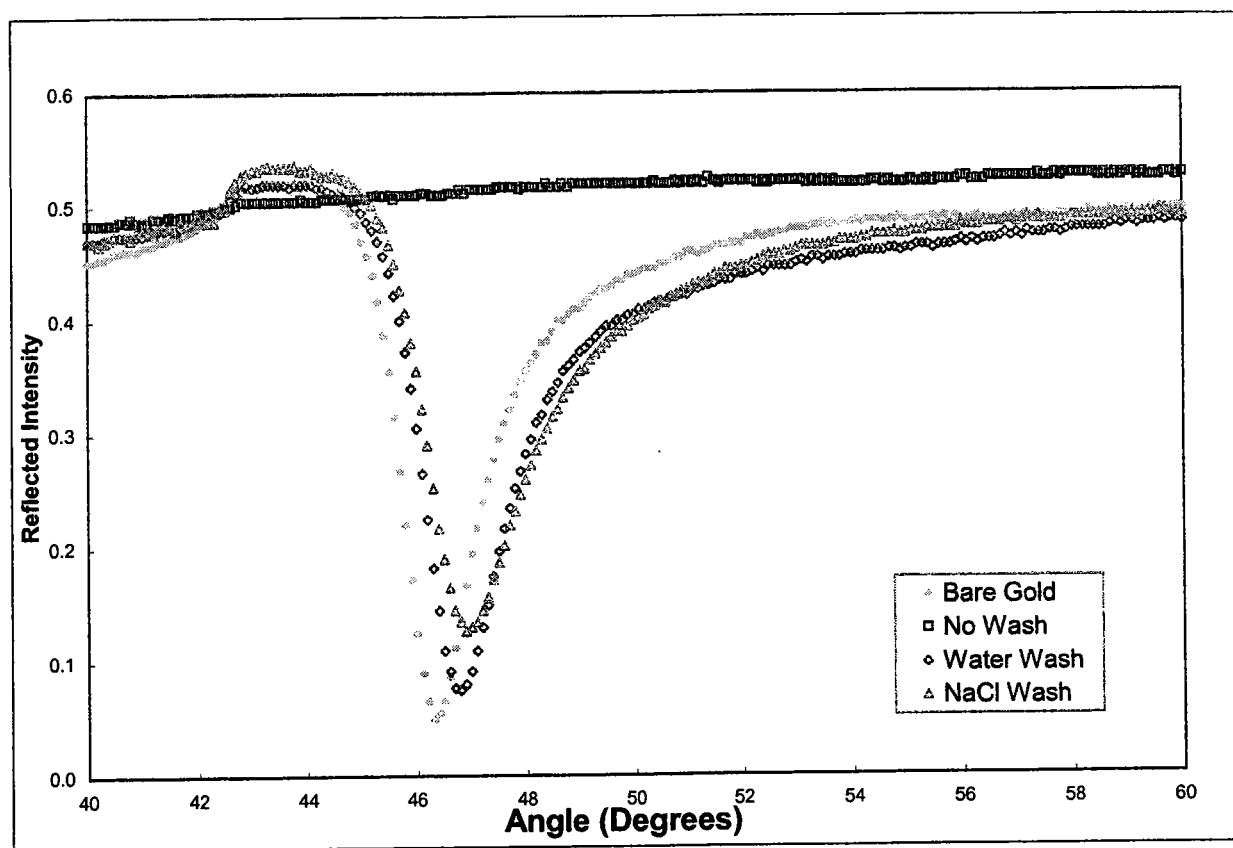


FIGURE 3: SPR spectra of uncoated gold substrate, additive coated gold and coated gold after washing with water and 1% NaCl solution.